Influences of Additives on Superconducting Properties and Crystallization Process of Bi-Sr-Ca-Cu-O Glass-Ceramics

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Bi-Sr-Ca-Cu-O 系ガラスセラミックスの超伝導特性と結晶化過程に関する添加物の影響

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The influences of additives such as Pb or Sb on the superconducting properties and crystallization process of Bi-Sr-Ca-Cu-O glass-ceramics were investigated. $T_c(\text{end})$ was influenced only by Pb, but not by K, Na, Sn, Sb or Li. The addition of Pb increased $T_c(\text{end})$ above 100 K. The results of differential thermal analysis and X-ray diffraction analysis showed that the addition of Pb, Sn or Pb and Sb enhanced crystallization of the superconducting phases, but no clear exothermic crystallization peak was observed in the samples containing K or Na oxide.

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1. Introduction

Since Bednorz and Müller first reported on the La-Ba-Cu-O system as a potential high- T_c superconducting oxide,¹⁾ many studies aiming to find high- T_c superconducting oxides have been carried out.²⁾⁻⁴⁾ Consequently, Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O with $T_c(\text{end}) > 100$ K was reported.^{3), 4)} In particular, Bi-Sr-Ca-Cu-O system has been extensively studied on account of its low toxicity, but this material frequently contains some other superconducting phases, resulting in a $T_c(\text{end})$ below 90 K.^{5), 6)}

As indicated in the previous papers,^{7), 8)} some compositions of the Bi-Sr-Ca-Cu-O system are glass-forming, and they show superconducting transition after proper annealing.⁷⁾⁻¹⁵⁾ However, the $T_c(\text{end})$ for the samples annealed from the completely glassy state can not be currently above 100 K in Bi-Sr-Ca-Cu-O glass-ceramics without any additives to the best of the authors' knowledge. Recently, Takano et al.¹⁶⁾ discovered the usefulness of the addition of PbO to produce the mostly single high- T_c phase ($T_c(\text{end}) > 100$ K) of bulk Bi, Pb-Sr-Ca-Cu-O. On the other hand, Endo et al.¹⁷⁾ noticed the significant role of the partial pressure of oxygen during annealing in eliminating low- T_c phases, and likewise obtained single high- T_c phase bulk specimens. From our previous work on Pb added

Bi-Sr-Ca-Cu-O glass-ceramics, the addition of Pb were proved to be likewise useful, and the heat-treatment under low oxygen partial pressure was also necessary to increase $T_c(\text{end})$ above 100 K ($T_c(\text{end}) = 102$ K) for superconducting glass-ceramics. This work reports the influences of the various additives including Pb on superconducting properties and crystallization process of the superconducting glass-ceramics.

2. Experimental procedure

Commercially available, analytical grade Bi_2O_3 , SrCO_3 , CaCO_3 and CuO were weighed out to the nominal compositions of $\text{BiSrCaCu}_2\text{O}_x$, and Sb_2O_5 , PbO , Li_2CO_3 , Na_2CO_3 , K_2CO_3 and mixed PbO and Sb_2O_5 were added in ratios of 0.1. The ratio of the additives was determined from the case for the highest $T_c(\text{end})$ in the PbO added Bi-Sr-Ca-Cu-O (BSCCO) glass-ceramics. The powders were mixed and melted in platinum crucibles at 1150°C for 30-40 min in an electric furnace in air. The melts were poured onto an stainless steel plate and pressed quickly. The obtained samples were annealed at 840°C for 150 h in $\text{Ar} : \text{O}_2 = 12 : 1$ and cooled down in the furnace. The thickness of the quenched samples was approximately 1.0 mm.

The temperature dependence was measured by a four-point probe technique at a constant dc

current. The resistivity at each temperature was measured for two opposite current directions, and superconducting transition curves were obtained from the mean values of the both increase and decrease of temperature procedures.

X-ray diffraction (XRD) patterns of samples without powdered were recorded by a JEOL JDX-10 X X-ray diffractometer from $2\theta = 3^\circ$ to 40° . Differential thermal analysis (DTA) was carried out by means of the Rigaku TG-DTA CN 80716 E1 at a heating rate of $20^\circ\text{C}/\text{min}$ from room temperature to 1100°C in air.

3. Results and discussion

Figure 1 shows some typical XRD patterns of as-quenched samples. As one can see, as-quenched samples except Na- or K-doped samples are amorphous by XRD. The electric properties of the as-quenched state for the current samples were insulating, and no superconducting transition could be seen above 10 K.

Figures 2 (1) and (2) show the differential thermal analysis (DTA) curves for the present systems. The results can be divided into two groups although the amount of the additives was only 2 mol% of cations. One has detectable glass transition temperature (T_g), one or two exothermic peaks around 550°C , and broad endothermic peak before the melting point. The other, in specific, Na- or K-doped samples, has no detectable glass transition temperature, one endothermic

Fig.1. X-ray diffraction patterns of as-quenched BSCCO with some additives.

(a) : PbO-doped, (b) : Li_2O -doped, (c) : SnO-doped

mic peak near 530°C , but has the similar thermal reaction above 600°C . The addition of Pb, Li, Sn or Pb, Sb lowered T_g compared to non-doped glass-ceramics, presumably enhancing atomic rearrangement. Practically, two exothermic peaks due to crystallization were observed for these samples, while only one peak was seen for non-doped.

The XRD measurements were carried out for all of the specimens after annealed just above the thermal reaction taking place and 800°C in air. Figures 3 (1), (2), and (3) correspond to XRD patterns of non-doped, Pb-doped and Pb, Sb-doped glass-ceramics. In Fig.3 (1), three relatively intense peaks are detectable after annealed at 600°C , and those can be assigned to

Fig.2. (1) DTA curves of BSCCO glasses with some additives. (a) : non-doped, (b) : PbO-doped.

T_g : glass transition temperature, T_x : crystallization temperature, and T_m : melting point.

(2) DTA curves of BSCCO glasses with some additives. (c) : Li-doped, (d) : Na-doped, (e) : K-doped, (f) : Sn-doped, and (g) Pb- and Sb-doped.

T_g : glass transition temperature, T_x : crystallization temperature, and T_m : melting point.

Fig. 3. (1) XRD patterns of non-doped glass-ceramics after annealed at 620°C (top) and at 800°C (bottom). The peaks of phase A ((Sr, Ca)₃Cu₅O_x-like or the very low- T_c phase), the low- T_c phase, CuO, Cu₂O, and CaO are shown by crosses, open triangles, open squares, solid triangle, and solid square, respectively. (2) XRD patterns of Pb-doped glass-ceramics after annealed at 570°C (top), (b) 620°C (middle), and (c) 800°C (bottom). The peaks of phase A ((Sr, Ca)₃Cu₅O_x-like or the very low- T_c phase), the low- T_c phase, CuO, Cu₂O, CaO, and unknown are shown by crosses, open triangles, open squares, solid triangles, solid square, and “*” marks, respectively. (3) XRD patterns of Pb- and Sb-doped glass-ceramics after annealed at 570°C (top), 620°C (middle), and 800°C (bottom). The peaks of phase A ((Sr, Ca)₃Cu₅O_x-like or the very low- T_c phase), the low- T_c phase, CuO, Cu₂O, CaO, and CaPbO₄ are shown by crosses, open triangles, open squares, solid triangle, solid square, and solid circles, respectively.

very low- T_c phase ($T_c(\text{end}) \sim 10$ K) or (Sr, Ca)₃Cu₅O_x-like crystal phase.⁸⁾ Hereafter, this phase will be named as phase A. Besides of the phase A, CuO, Cu₂O and CaO were also formed. After annealing at 800°C, phase A was transformed to low- T_c phase ($T_c(\text{end}) \sim 75$ K). Fig. 3 (2) shows the XRD patterns of a Pb-doped sample annealed at 570°C, and 800°C from the top to the bottom, respectively. Compared to Fig. 3 (1), the peaks of the phase A were sharpened and even the number of the peaks was increased, and that this tendency was enhanced further by the annealing at 620°C. Thus, it can be said that the addition of Pb enhanced crystallization of the first phase from the amorphous state. At 800°C, the phase A was likewise transformed to the low- T_c phase. The addition of Pb and Sb also enhanced crystallization, but some impurity phases such as CaPbO₄ were formed as seen in Fig. 3 (3). The second exothermic peak seems to be mainly due to the oxidization of Cu₂O to CuO since no other remarkable difference could be found between the patterns. After annealed at

800°C, the phase A was similarly converted to the low- T_c phase.

Figures 4 (1), (2), (3), and (4) are XRD patterns of Li-doped, Na-doped, K-doped and Sn-doped BSCCO glass-ceramics after heated just above the thermal reactions taking place or at 800°C in air, respectively. In Fig. 4 (1), the formation of phase A was observed at 570°C, and the pattern itself was similar to the non-doped after annealed at 620°C. Figures 4 (2) and (3) show XRD data for Na- and K-doped glass-ceramics, respectively. For these samples after heated at 570°C, phase A was mainly formed, but, in particular for K-doped specimen, the peaks were broad and weak compared with others. Since the as-quenched bodies contained crystal particles, the endothermic peak in DTA might be caused by the conversion of the original crystal phases to others seen in Fig. 4. Moreover, Fig. 4 (3) indicates the addition of K even disturbs the crystal growth of phase A, most likely by the ionic diffusion. From Fig. 4 (4), one can say the influence of the Sn doping is similar to those

Fig. 4. (1) XRD patterns of Li-doped glass-ceramics after heated at 570°C (top), 620°C (middle), and 800°C (bottom). The peaks of phase A ((Sr, Ca)₃Cu₅O_x-like or the very low- T_c phase), the low- T_c phase, CuO, Cu₂O, and CaO are shown by crosses, open triangles, open squares, solid triangle, and solid squares, respectively.

(2) XRD patterns of Na-doped glass-ceramics after heated at 570°C (top) and 800°C (bottom). The peaks of phase A ((Sr, Ca)₃Cu₅O_x-like or the very low- T_c phase), the low- T_c phase, CuO, Cu₂O, and CaO are shown by crosses, open triangles, open squares, solid triangle, and solid squares, respectively.

(3) XRD patterns of K-doped glass-ceramics after heated at 570°C (top), 620°C (middle), and 800°C (bottom). The peaks of phase A ((Sr, Ca)₃Cu₅O_x-like or the very low- T_c phase), the low- T_c phase, CuO, Cu₂O, and CaO are shown by crosses, open triangles, open squares, solid triangle, and solid square, respectively.

(4) XRD patterns of Sn-doped glass-ceramics after heated at 570°C (top), 620°C (middle), and 800°C (bottom). The peaks of phase A ((Sr, Ca)₃Cu₅O_x-like or the very low- T_c phase), the low- T_c phase, CuO, Cu₂O, CaO, and unknown are shown by crosses, open triangles, open squares, solid triangle, solid square, and "*" marks, respectively.

Fig. 5. (1) XRD patterns of non-doped (1), Pb-doped (2), K-doped (3) and Na-doped (4) BSCCO glass-ceramics after heated at 840°C for 150 h in Ar : O₂ = 12 : 1 atmosphere. The peaks of the high- T_c phase, low- T_c phase, CuO and unknown phase are shown by open circles, open triangles, open squares and "*" marks, respectively. (2) XRD patterns of Li-doped (5), Sn-doped (6) and Pb, Sb-doped (7) BSCCO glass-ceramics after heated at 840°C for 150 h in Ar : O₂ = 12 : 1 atmosphere. The peaks of the low- T_c phase, Cu₂O and unknown phase are shown by open triangles, solid triangles and "*" marks, respectively.

Fig. 6. (1) Temperature dependence of dc resistance of the derived non-doped (open circles), Pb-doped ("*" marks), K-doped (open squares) and Na-doped (open triangles) BSCCO glass-ceramics. The resistance was shown as $R(T)/R(300\text{K})$, where $R(T)$ is the resistance at $T\text{K}$ and $R(300)$ is that at 300 K. (2) Temperature dependence of dc resistance of the derived Li-doped (open circles), Sn-doped (open squares) and Pb, Sb-doped (open triangles) BSCCO glass-ceramics. The resistance was shown as $R(T)/R(300\text{K})$, where $R(T)$ is the resistance at $T\text{K}$ and $R(300)$ is that at 300 K.

of Pb, and Pb, Sb. The phase A after annealed at 570°C or 620°C were sharp and intense, but with intense peak of impurity. The phase remained even after heated at 800°C.

Figures 5 (1) and (2) correspond to the XRD patterns of each glass-ceramics after heated at 840°C for 150 h in Ar : O₂ = 12 : 1 atmosphere. For non-doped glass-ceramics, predominant phase was the low- T_c phase and small amount of CuO. The high- T_c phase ($T_{c(\text{end})}$ = 105 K) was observed in Pb-doped BSCCO glass-ceramics (Fig. 5 (1)). The approximate concentration of the high- T_c phase was 65% estimated from (002) reflection lines. The predominant phase in others was the low- T_c phase, but some differences can be seen among them. The preferential orientation of crystalline phase can be noticed in K- or Li-doped glass-ceramics. For both samples, (00 n), where n is integer, reflection lines were rather intense compared to others, and thus c -axis

of the superconducting phase preferentially oriented to the pressed direction in quenching. On the other hand, (11 n) and (n 00) reflection lines of Na-doped and Pb, Sb-doped glass-ceramics were pointed out. Compared to non-doped glass-ceramics, the addition of oxides with relatively low melting point may greatly influence the crystal growth mechanism in amorphous state. For Sn-doped glass-ceramics, some peaks from unknown impurity phase were found even heated in low oxygen atmosphere at 840°C, and no (002) reflection line could be detected.

Figures 6 (1) and (2) show temperature dependence of dc conductivity for each glass-ceramics after heated at 840°C in Ar : O₂=12 : 1 atmosphere for 150 h. For non-doped glass-ceramics, T_c (onset) was 90 K and T_c (end) was 78 K, and no drastic drop of the resistance could be seen above 100 K. Thus, even from electric properties, no formation of high- T_c phase could be seen. The Pb addition increased T_c (onset) and T_c (end) to 120 K and 102 K, respectively. To the best of the authors' knowledge for BSCCO glass-ceramics, these are the highest values, and no influences of the alumina contamination from the crucibles used in the previous paper⁸⁾ on T_c (end) was observed. The temperature dependence of dc conductivity for K-doped, Na-doped, Li-doped, and Sn-doped ((3), (4), (5) and (6)) were quite close to non-doped glass-ceramics in (1), although the addition of them influenced preferential crystal orientation or crystallization processes to a large degree. T_c (onset) and T_c (end) values of K-doped, Na-doped, Li-doped, and Sn-doped glass-ceramics were 92 K and 78 K, 90 K and 78 K, 92 K and 79 K, and 90 K and 75 K, respectively, and no drop in the resistance could be seen above 100 K. Therefore, no high- T_c phase formation could be found even from the electrical properties. On the other hand, two steps in the superconducting transition were noticed in Pb, Sb-doped glass-ceramics ((7)). T_c (onset) was 114 K and T_c (end) was 75 K. Thus, the some portion of the glass-ceramics was proved to be the high- T_c phase. The first drop correspond to 50% of the total drop of the resistance in the transition, but no new super high- T_c phase (T_c (end)>120 K) could be found.

4. Conclusion

(1) Among the present samples, non-doped, Pb-doped, Li-doped, Sn-doped and Pb, Sb-doped system were glass-formable.

(2) From DTA studies, two exothermic crystallization peaks were found for Pb-, Pb, Sb-, Li- or Sn-doped glass-ceramics just above

T_g , where one endothermic peak were observed for Na- or K-doped.

(3) The main crystal phase formed near 550°C and 800°C were phase A and the low- T_c phase, but the crystallinity was dependent on the additives. In specific, Pb, Sn, and Pb, Sb seem to enhance crystallization of phase A, while K seems to retard it.

(4) Crystal orientation was likewise largely influenced by the additives.

(5) Regarding on the superconducting transition, only Pb-doped BSCCO glass-ceramics had relatively large portion of high- T_c phase with T_c (end) above 100 K (102 K), and Pb, Sb-doped glass-ceramics showed two steps of the transition, resulting from the partial formation of the high- T_c phase. On the other hand, for non-doped and other oxides-doped glass-ceramics, the superconducting transition was predominantly determined by the low- T_c phase, and thus no remarkable influences could be seen on T_c (end).

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References

- 1) J. G. Bednorz and K. A. Müller, *Z. Phys.*, **B 64**, 189-90 (1986).
- 2) M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang and C. W. Chu, *Phys. Rev. Lett.*, **58**, 908-10 (1987).
- 3) H. Maeda, Y. Tanaka, M. Fukutomi and T. Asano, *Jpn. J. Appl. Phys.*, **27**, L 209-10 (1988).
- 4) Z. Z. Sheng, A. M. Hermann, A. El Ali, C. Almasan, J. Estrada and T. Datta, *Phys. Rev. Lett.*, **60**, 937-39 (1988).
- 5) N. Kijima, H. Endo, J. Tsuchiya, A. Sumiyama, M. Mizuno and Y. Oguri, *Jpn. J. Appl. Phys.*, **27**, L 821-23 (1988).
- 6) D. Shindo, K. Hiraga, M. Hirabayashi, M. Kikuchi and Y. Syono, *Jpn. J. Appl. Phys.*, **27**, L 1018-21 (1988).
- 7) H. Nasu, Y. Ibara, S. Makida, T. Imura and Y. Osaka, *J. Non-Cryst. Solids.*, **105**, 185-87 (1988).
- 8) Y. Ibara, H. Nasu, T. Imura and Y. Osaka, *Jpn. J. Appl. Phys.*, **28**, L 37-40 (1989).
- 9) T. Komatsu, R. Sato, K. Imai, K. Matusita and T. Yamashita, *Jpn. J. Appl. Phys.*, **27**, L 550-52 (1988).
- 10) A. Inoue, H. Kimura, K. Matsuzaki, A-P. Tsai and T. Masumoto, *Jpn. J. Appl. Phys.*, **27**, L 941-43 (1988).
- 11) T. Komatsu, K. Imai, R. Sato, K. Matusita and T. Yamashita, *Jpn. J. Appl. Phys.*, **27**, L 533-35 (1988).
- 12) T. Minami, Y. Akamatsu, M. Tatsumisago, N. Tohge and Y. Kowada, *Jpn. J. Appl. Phys.*, **27**, L 777-78 (1988).
- 13) T. Komatsu, R. Sato, K. Matusita and T. Yamashita, *Jpn. J. Appl. Phys.*, **27**, L 1839-42 (1988).

- 14) M. Yoshimura, T.-H. Sung, Z. Nakagawa and T. Nakamura, *Jpn. J. Appl. Phys.*, **27**, L 1877-79 (1988).
 - 15) Y. Abe, H. Hosono, M. Hosoe, J. Iwase and Y. Kubo, *Appl. Phys. Lett.*, **53**, 1341-43 (1988).
 - 16) M. Takano, J. Takada, K. Oda, H. Kitaguchi, Y. Miura, Y. Ikeda, Y. Tomii and H. Mazaki, *Jpn. J. Appl. Phys.*, **27**, L 1041-43 (1988).
 - 17) W. Endo, S. Koyama and T. Kawai, *Jpn. J. Appl. Phys.*, **27**, L 1476-79 (1988).
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